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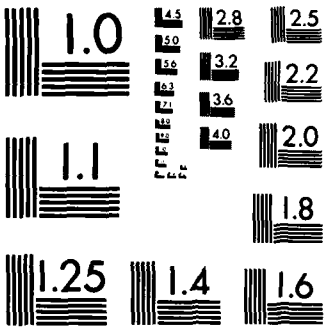

MICROCOPY RESOLUTION TEST CHART
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The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An investigation of layers of CuCl grown on the (III) face of silicon has been undertaken. Detailed studies using ESCA for analysis have led to the development of an effective etching and cleaning procedure for silicon surfaces. CuCl layers can not be grown by vapor phase transport, nor from liquid fluxes using a dipping technique, but polycrystalline layers may be grown using an improved slider-boat technique. The CuCl/silicon specimens exhibit a dielectric anomaly.

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20. Abstract continued

The temperature of the onset of the dielectric anomaly varies from specimen to specimen, and it also depends on the history of the specimen. Materials research designed to determine the factors which affect this phenomenon is underway.

INVESTIGATIONS OF PHASE TRANSITIONS

FINAL REPORT

WILLIAM E. HATFIELD

AUGUST 12, 1985

U. S. ARMY RESEARCH OFFICE

CONTRACT NO. DAAG29-79-D-1002

UNIVERSITY OF NORTH CAROLINA

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STATEMENT OF THE PROBLEM

This program is devoted to the study of phase transition in inorganic solids by measurement of dielectric properties and magnetic properties as a function of temperature. Phenomena occurring as a result of experimental conditions such as substrate, molten salt flux composition, external magnetic fields, and layer thickness are studied systematically.

In this phase of the program, the major emphasis of the work was devoted to the production of epitaxial layers of CuCl on silicon. Techniques employed included vapor phase deposition, with and without transport gas, and liquid phase epitaxy from molten salt fluxes, by the dipping technique and by the slider boat technique. Specimens produced by these techniques were characterized by ESCA spectroscopy, dielectric measurements, magnetic susceptibility measurements, electron paramagnetic resonance spectroscopy, and Rutherford back scattering.

Summary of Important Results

Previous results have shown that there are giant diamagnetic anomalies in disordered CuCl in the temperture range 77 to 280 K under applied pressures greater than 5 kbar. The diamagnetic anomaly has been explained in terms of an exciton, but it has not been possible to reproduce the experimental results consistently. It has further been postulated that the unusual behavior was a property of a new form of CuCl. This new form of

CuCl is said to be uneffected by the laboratory atmosphere. It was further postulated that a new form of CuCl may occur as epitaxially grown layers on silicon.

In this phase of the research program, it was found that it is not possible to grow epitaxial layers of CuCl on silicon by vapor phase deposition. Either with or without a transport gas, in this case argon, CuCl decomposes and deposits crystallites of copper metal on the silicon in the growth apparatus. In addition, there is a reaction of the gaseous CuCl and decomposition products with the silicon to yield a white powder. The white powder was not identified.

A systematic study of etch and cleaning procedures was undertaken. The most effective etching method is as follows: The first step in the etching and cleaning procedure was a preoxidation step using a solution of sulfuric acid and hydrogen peroxide to remove organic contaminants. The silicon wafer was then exposed to a vapor of hydrogen fluoride above a concentrated hydrogen fluoride solution inside a closed container. This step removed the native oxide layer. The specimens were not rinsed after vapor HF treatment, but instead the silicon wafer was immediately placed in the cleaning solutions. The first cleaning solution was an aqueous solution of ammonium hydroxide and hydrogen peroxide. This mixture was found to be more effective for removal of heavy metal contaminants than was a hydrochloric acid-peroxide mixture. After a distilled-

dionized water rinse, a cleaning solution of hydrogen chloride, hydrogen peroxide, and water was used to remove lighter contaminants. The final water rinse was followed by drying under dry, cold, nitrogen gas prior to insertion of the silicon into the growth apparatus. Specimens prepared in this manner were submitted for ESCA analysis, and contaminants and oxides were proven to have been removed.

It had been reported that CuCl could be epitaxially grown on silicon wafers by a dipping technique in a flux. Considerable effort was expended in designing a dipping chamber in which the temperature of the flux and the atmosphere above the molten salt could be controlled precisely.

ESCA analyses of CuCl/silicon specimens produced by this technique showed that the specimens were heavily contaminated with the flux components. Because of the contamination problem, it is clear that the dipping technique will not work for the growth of epitaxial layers of CuCl on silicon.

A new design for a a slider boat for liquid phase epitaxy was developed, and the boat constructed. The boat was used successfully for the preparation of CuCl/silicon specimens. The thickness of the CuCl layer could be controlled and layers ranging from a few hundred Å's to a few thousand Å's were produced. ESCA analyses of these specimens did not reveal contaminants from the growth flux. Rutherford backscattering using helium ions proved that the layers were polycrystalline.

Capacitance measurements, made in the range 77 to 300 K, revealed dielectric anomalies in the same temperature range as the giant diamagnetic anomaly that had been observed previously. The temperature at which the dielectric anomaly occurred varied from sample to sample, and it was dependent on the history of the sample. It was concluded that the temperature cycling produced stresses in the CuCl layers, and that these stresses affected the dielectric anamoly.

Thus, unusual behavior has been observed in single crystals of CuCl under light radiation, on amorphorous sample of CuCl under pressure, and, now, on CuCl layers epitaxially grown on silicon. The phenomena occurring in the single crystals and amorphorous state are difficult to reproduce. However, the anomaly in the dielectric behavior of the CuCl/silicon specimens occurs consistently. In this case, however, the temperature of the onset of the dielectric anomaly is dependent on the specimen and its history. More detailed materials research designed to identify the materials parameters which effect this anomaly are under way.

LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

Dr. William E. Hatfield	Department of Chemistry University of North Carolina
Mr. M. Wayne Pickens	Department of Chemistry University of North Carolina Candidate for Ph.D. degree
Dr. P.B. Sczaniecki	Present Address: Institute of Molecular Physics Poznan, Poland Research Associate
Mr. J. M. Waller, Jr.	Department of Chemistry University of North Carolina Research Assistant
Mr J. E. Jaynes	Department of Physics University of North Carolina Reserch Assistant

LIST OF PUBLICATIONS AND REPORTS

"The Production and Analysis of Cuprous Chloride on Silicon"; Ph.D. Dissertation, Department of Chemistry, University of North Carolina; 1985 (in preparation).

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